



(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 630 964 B1

(12)

## EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention  
of the grant of the patent:  
**05.08.1998 Bulletin 1998/32**

(51) Int Cl. 6: **C11D 3/34, C11D 3/26,**  
**C11D 3/32, C11D 3/39,**  
**C07F 13/00, C07C 251/24,**  
**C07C 281/14, C07C 309/49**

(21) Application number: **94810345.2**

(22) Date of filing: **10.06.1994**

### (54) Inhibition of re-absorption of migrating dyes in the wash liquor

Inhibierung der Wiederabsorption von migrierenden Farbstoffen in der Waschlösung

Inhibition de la réadsorption des colorants migrants dans le liquide lessiviel

(84) Designated Contracting States:  
**AT BE CH DE DK ES FR GB GR IT LI NL PT SE**

(72) Inventors:

- Eckhardt, Claude, Dr.  
F-68400 Riedisheim (FR)
- Reinehr, Dieter, Dr.  
D-79400 Kandern (DE)

(30) Priority: **19.06.1993 GB 9312693**  
**08.12.1993 GB 9325117**

(56) References cited:

<b>EP-A- 0 538 228</b>	<b>WO-A-91/14694</b>
<b>WO-A-93/03838</b>	<b>US-A- 3 173 956</b>
<b>US-A- 4 655 785</b>	

(43) Date of publication of application:  
**28.12.1994 Bulletin 1994/52**

(73) Proprietor: **Ciba Specialty Chemicals Holding Inc.**  
**4057 Basel (CH)**

EP 0 630 964 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

**Description**

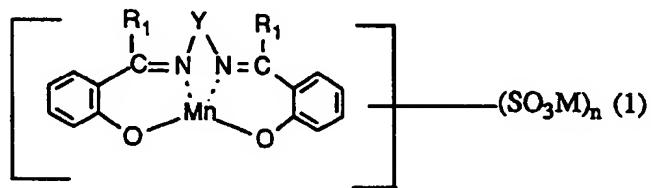
The present invention relates to a process for inhibiting the re-absorption of migrating dyes in the wash liquor.

It is well known that various metal compounds, e.g. manganese complexes, are useful in detergents as catalysts for peroxides.

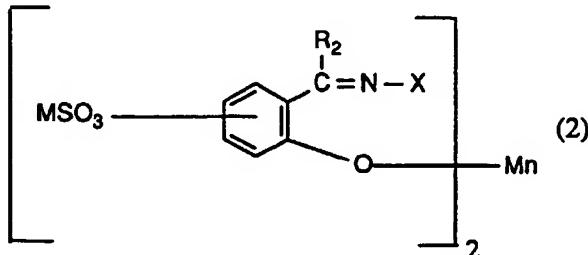
It has now been found that certain other manganese complexes, although effecting no apparent improvement in the bleaching power of peroxides, exert a pronounced bleaching effect on dirt or dyes in the wash bath. Moreover, these manganese complexes do not exhaust at all on to cotton, polyamide or polyester fibres so that the complexes cannot lead to fibre discolouration problems.

Accordingly, the present invention provides a process for inhibiting the re-absorption of migrating dyes in the wash liquor, comprising introducing into a wash liquor containing a peroxide-containing detergent, from 0.5 to 150, preferably from 1.5 to 75, especially from 7.5 to 40 mg, per litre of wash liquor, of one or more compounds having the formula (1), (2), (3), (4), (5), (6) or (7):

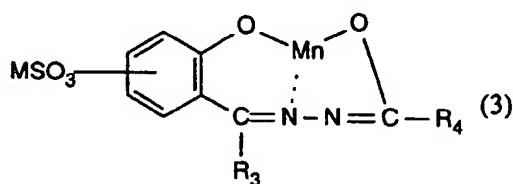
15



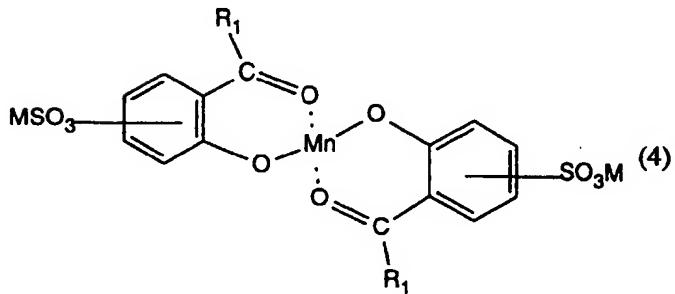
25

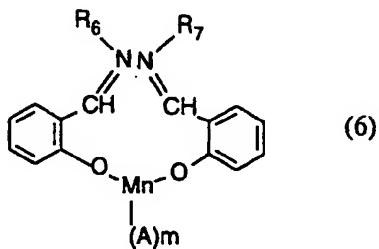
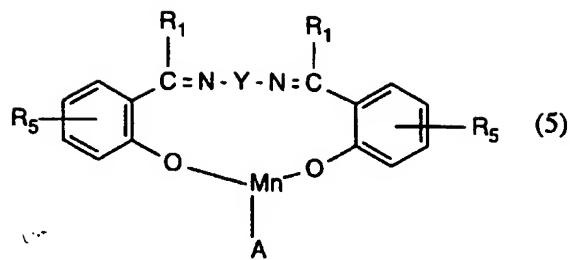


35

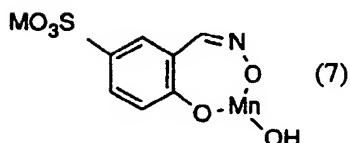


45





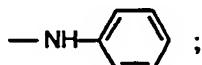
25 or



35 in which R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are the same or different and each is hydrogen or optionally substituted alkyl, cycloalkyl or aryl; R<sub>5</sub> is hydrogen, alkyl or SO<sub>3</sub>M; R<sub>6</sub> and R<sub>7</sub> are the same or different and each is NH-CO-NH<sub>2</sub>, a group of formula



45 or a group of formula



50 Y is optionally substituted alkylene or cyclohexylene; X is OH, NH<sub>2</sub>, optionally substituted aryl or optionally substituted alkyl; n is 0, 1, 2 or 3; M is hydrogen, an alkali metal atom, ammonium or a cation formed from an amine; m is 0 or 1; and A is an anion.

55 When one or more of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub> and X are optionally substituted alkyl, preferred alkyl groups are C<sub>1</sub>-C<sub>8</sub>, especially C<sub>1</sub>-C<sub>4</sub>-alkyl groups. The alkyl groups may be branched or unbranched and may be optionally substituted, e.g. by halogen such as fluorine, chlorine or bromine, by C<sub>1</sub>-C<sub>4</sub>-alkoxy such as methoxy or ethoxy, by phenyl or carboxyl, by C<sub>1</sub>-C<sub>4</sub>-alkoxycarbonyl such as acetyl, or by a mono- or di-alkylated amino group.

When one or more of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> and R<sub>5</sub> are cycloalkyl, this may also be substituted, e.g. by C<sub>1</sub>-C<sub>4</sub>-alkyl or C<sub>1</sub>-

C<sub>4</sub>-alkoxy.

When one or more of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub> and X are optionally substituted aryl, they are preferably a phenyl or naphthyl group which may be substituted by C<sub>1</sub>-C<sub>4</sub>-alkyl, e.g. by methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec.-butyl or tert.-butyl, by C<sub>1</sub>-C<sub>4</sub>-alkoxy such as methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, sec.-butoxy or tert.-butoxy, by halogen such as fluorine, chlorine or bromine, by C<sub>2</sub>-C<sub>5</sub>-alkanoylamino, such as acetylarnino, propionylarnino or butyrylarnino, by nitro, sulpho or by dialkylated amino.

When Y is alkylene, it is preferably a C<sub>2</sub>-C<sub>4</sub>-alkylene residue, especially a -CH<sub>2</sub>-CH<sub>2</sub>-bridge. Y may also be a C<sub>2</sub>-C<sub>8</sub>-alkylene residue which is interrupted by oxygen or, especially, by nitrogen, in particular the -(CH<sub>2</sub>)<sub>3</sub>-NH-(CH<sub>2</sub>)<sub>3</sub>-bridge.

10 Anions A include halide, especially chloride, sulphate, nitrate, hydroxy, methoxy, BF<sub>4</sub>, PF<sub>6</sub>, carboxylate, especially acetate, triflate or tosylate.

With respect to the compounds of formula (1), preferably each R<sub>1</sub> is hydrogen, Y is the ethylene bridge and n is 2, whereby one sulpho group is preferably present in each benzene ring, especially in para position to the oxygen atom.

In relation to the compounds of formula (2), preferably R<sub>2</sub> is hydrogen and X is OH.

15 With respect to the compounds of formula (3), preferred compounds are those in which R<sub>3</sub> is hydrogen and R<sub>4</sub> is hydrogen, methyl or, especially, phenyl. Especially preferred compounds are those in which the SO<sub>3</sub>M group is in para position to the oxygen atom.

With respect to the compounds of formula (4), preferred compounds are those in which R<sub>1</sub> is hydrogen, more especially those in which each SO<sub>3</sub>M group is in para position to the respective oxygen atom.

20 As to the compounds of formula (5), preferably R<sub>1</sub> is hydrogen or methyl, R<sub>5</sub> is hydrogen, methyl or SO<sub>3</sub>Na and is preferably in p-position with respect to the oxygen atom, Y is -CH<sub>2</sub>CH<sub>2</sub>- or cyclohexylene and A is a chloride, acetate, hydroxy, methoxy or PF<sub>6</sub> anion.

In relation to the compounds of formula (6), preferably R<sub>6</sub> and R<sub>7</sub> are the same. The preferred anion, when present, is acetate.

25 In each of the compounds of formula (1) to (7), it is preferred that they are used in neutral form, i.e. that M, when present, is other than hydrogen, preferably a cation formed from an alkali metal, in particular sodium, or from an amine.

Moreover, in each of the compounds of formula (1) to (7), the respective benzene rings may contain, in addition to any sulpho group, one or more further substituents such as C<sub>1</sub>-C<sub>4</sub>-alkyl, C<sub>1</sub>-C<sub>4</sub>-alkoxy, halogen, cyano or nitro.

30 Many of the manganese complexes of formula (2) and (4) to (7) are believed to be new compounds and such new compounds form a further aspect of the present invention. They may be produced by known methods, e.g. by the methods analogous to those disclosed in US Patent 4,655,785 relating to similar copper complexes.

Other references which describe similar manganese complexes are WO 91/14694 and WO 93/03838 which each disclose, *inter alia*, manganese complexes similar to those of formula (5) of the present invention, as well as their use as catalysts in epoxidation reactions; US 3,173,956 which describes a process for the production of salicylaldehyde by oxidizing certain intermediates which appear to bear some similarity to manganese complexes of formula (5) of the present invention; and EP-A-538,228 which discloses a dye transfer inhibiting composition comprising a metallo catalyst selected from a metallo porphin, a metallo porphyrin and a metallo phthalocyanine.

The present invention also provides a detergent composition comprising:

40 i) 5-90%, preferably 5-70% of A) an anionic surfactant and/or B) a nonionic surfactant;  
 ii) 5-70%, preferably 5-50%, especially 5-40% of C) a builder;  
 iii) 0.1-30%, preferably 1-12% of D) a peroxide; and  
 iv) 0.005-2%, preferably 0.02-1%, especially 0.1-0.5% of E) a compound of formula (1) to (7) as defined above, each by weight, based on the total weight of the detergent.

45 The detergent may be formulated as a solid; or as a non-aqueous liquid detergent, containing not more than 5, preferably 0-1 wt.% of water, and based on a suspension of a builder in a non-ionic surfactant, as described, e.g., in GB-A-2158454.

Preferably, the detergent is in powder or granulate form.

50 Such powder or granulate forms may be produced by firstly forming a base powder by spray-drying an aqueous slurry containing all the said components, apart from the components D) and E); then adding the components D) and E) by dry-blending them into the base powder. In a further process, the component E) may be added to an aqueous slurry containing components A), B) and C), followed by spray-drying the slurry prior to dry-blending component D) into the mixture. In a still further process, component B) is not present, or is only partly present in an aqueous slurry containing components A) and C); component E) is incorporated into component B), which is then added to the spray-dried base powder; and finally component D) is dry-blended into the mixture.

The anionic surfactant component A) may be, e.g., a sulphate, sulphonate or carboxylate surfactant, or a mixture of these.

Preferred sulphates are alkyl sulphates having 12-22 carbon atoms in the alkyl radical, optionally in combination with alkyl ethoxy sulphates having 10-20 carbon atoms in the alkyl radical.

Preferred sulphonates include alkyl benzene sulphonates having 9-15 carbon atoms in the alkyl radical.

In each case, the cation is preferably an alkali metal, especially sodium.

Preferred carboxylates are alkali metal sarcosinates of formula  $R-CO(R^1)CH_2COOM^1$  in which R is alkyl or alkenyl having 9-17 carbon atoms in the alkyl or alkenyl radical,  $R^1$  is  $C_1-C_4$  alkyl and  $M^1$  is alkali metal.

The nonionic surfactant component B) may be, e.g., a condensate of ethylene oxide with a  $C_9-C_{15}$  primary alcohol having 3-8 moles of ethylene oxide per mole.

The builder component C) may be an alkali metal phosphate, especially a tripolyphosphate; a carbonate or bicarbonate, especially the sodium salts thereof; a silicate; an aluminosilicate; a polycarboxylate; a polycarboxylic acid; an organic phosphonate; or an aminoalkylene poly (alkylene phosphonate); or a mixture of these.

Preferred silicates are crystalline layered sodium silicates of the formula  $NaHSi_mO_{2m+1} \cdot pH_2O$  or  $Na_2Si_mO_{2m+1} \cdot pH_2O$  in which m is a number from 1.9 to 4 and p is 0 to 20.

Preferred aluminosilicates are the commercially-available synthetic materials designated as Zeolites A, B, X, and HS, or mixtures of these. Zeolite A is preferred.

Preferred polycarboxylates include hydroxypolycarboxylates, in particular citrates, polyacrylates and their copolymers with maleic anhydride.

Preferred polycarboxylic acids include nitrilotriacetic acid and ethylene diamine tetra-acetic acid.

Preferred organic phosphonates or aminoalkylene poly (alkylene phosphonates) are alkali metal ethane 1-hydroxy diphosphonates, nitrilo trimethylene phosphonates, ethylene diamine tetra methylene phosphonates and diethylene triamine penta methylene phosphonates.

The peroxide component D) may be any organic or inorganic peroxide compound, described in the literature or available on the market, which bleaches textiles at conventional washing temperatures, e.g. temperatures in the range of from 10°C. to 90°C. In particular, the organic peroxides are, for example, monoperoxides or polyperoxides having alkyl chains of at least 3, preferably 6 to 20, carbon atoms; in particular diperoxydicarboxylates having 6 to 12 C atoms, such as diperoxypiperazates, diperoxypersubacetates, diperoxypthalates and/or diperoxododecanedioates, especially their corresponding free acids, are of interest. It is preferred, however, to employ very active inorganic peroxides, such as persulphate, perborate and/or percarbonate. It is, of course, also possible to employ mixtures of organic and/or inorganic peroxides.

The addition of the peroxides to the detergent is effected, in particular, by mixing the components, for example by means of screw-metering systems and/or fluidized bed mixers.

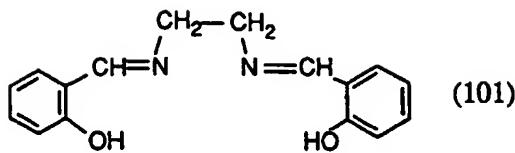
The detergents may contain, in addition to the combination according to the invention, one or more of fluorescent whitening agents, such as a bis-triazinylamino-stilbene-disulphonic acid, a bis-triazolyl-stilbene-disulphonic acid, a bis-styryl-biphenyl, a bis-benzofuranyl biphenyl, a bis-benzoxazyl derivative, a bis-benzimidazolyl derivative, a coumarine derivative or a pyrazoline derivative; soil suspending agents, for example sodium carboxymethylcellulose; salts for adjusting the pH, for example alkali or alkaline earth metal silicates; foam regulators, for example soap; salts for adjusting the spray drying and granulating properties, for example sodium sulphate; perfumes; and also, if appropriate, antistatic and softening agents; such as smectite clays; enzymes, such as amylases; photobleaching agents; pigments; and/or shading agents. These constituents should, of course, be stable to the bleaching system employed.

A particularly preferred detergent co-additive is a polymer known to be useful in preventing the transfer of labile dyes between fabrics during the washing cycle. Preferred examples of such polymers are polyvinyl pyrrolidones, optionally modified by the inclusion of an anionic or cationic substituent, especially those having a molecular weight in the range from 5000 to 60,000, in particular from 10,00 to 50,000. Preferably, such polymer is used in an amount ranging from 0.05 to 5%, preferably 0.2-1.7% by weight, based on the weight of the detergent.

The following Examples serve to illustrate the invention; parts and percentages are by weight, unless otherwise stated.

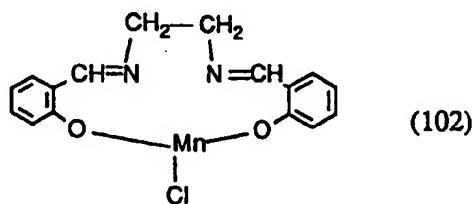
#### Example 1

60g of ethylenediamine are dropped into a solution of 277g of salicylaldehyde in 500ml of ethanol over 1 hour at 60°C. Stirring is continued at 60°C. for a further 2 hours and the precipitate so formed is filtered off. There are obtained 260g of a yellow compound having the formula:



corresponding to a yield of 97% of theory.

10 To 13.4g of the compound of formula (101) dissolved in 1000ml of ethanol there are added 12.25g of manganese-(II)-acetate.4H<sub>2</sub>O. The dark brown solution so produced is stirred at 75°C. for 3 hours and then evaporated to dryness. The residue is dissolved in 1250 ml of water, filtered and the filtrate is treated with 58g of NaCl. The precipitated dark brown product is filtered off and dried in vacuum. There are obtained 12.6g of the compound having the formula:



25 corresponding to a yield of 64% of theory.

Elemental analysis of the compound having the formula (102) and having the empirical formula C<sub>16</sub>H<sub>14</sub>ClMnN<sub>2</sub>O<sub>2</sub>.1.92H<sub>2</sub>O gives:

30

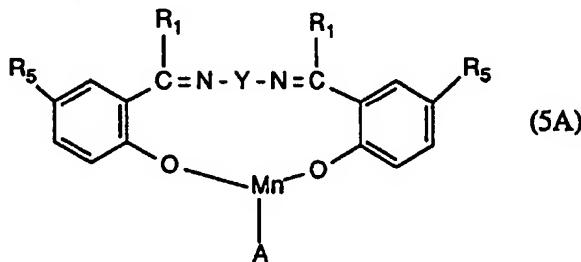
Req.%	C 49.11;	H 4.60;	N 7.16;	Cl 9.06;	H <sub>2</sub> O 8.84;	Mn 14.0.
Found %	C 49.4;	H 4.6;	N 7.1;	Cl 8.9;	H <sub>2</sub> O 8.82;	Mn 13.9.

### Example 2

35 The procedure described in Example 1 is repeated except that 14.1g of manganese-(III)-acetate.2H<sub>2</sub>O are used instead of 12.25g of manganese-(II)-acetate.4H<sub>2</sub>O. After working up, there are obtained 16g of the compound of formula (102) corresponding to a yield of 81.6% of theory.

### Examples 3 to 12

40 Using the procedure described in Example 1, the following compounds of formula (5A) are prepared:



55 Example 3 (compound 103):

R<sub>1</sub> is H; R<sub>5</sub> is H; Y is -CH<sub>2</sub>CH<sub>2</sub>-; and A is CH<sub>3</sub>COO.

Elemental analysis of the compound having the formula (103) and having the empirical formula C<sub>18</sub>H<sub>17</sub>MnN<sub>2</sub>O<sub>4</sub>

EP 0 630 964 B1

gives:

Req.%	C 56.8;	H 4.5;	N 7.4;	Mn 14.5.
Found %	C 56.7;	H 4.6;	N 7.3;	Mn 14.6.

5

Example 4 (compound 104):

$R_1$  is H;  $R_5$  is H; Y is  $-CH_2CH_2-$ ; and A is  $PF_6^-$ .

10 Elemental analysis of the compound having the formula (104) and having the empirical formula  $C_{16}H_{14}F_6MnN_2O_2P \cdot 2.12H_2O$  gives:

Req.%	C 38.1;	H 3.6;	N 5.6;	$H_2O$ 7.6;	Mn 10.9.
Found %	C 38.5;	H 3.5;	N 5.7;	$H_2O$ 7.6;	Mn 11.0.

15

Example 5 (compound 105):

$R_1$  is H;  $R_5$  is H; Y is 1,2-cyclohexylene; and A is  $CH_3COO^-$ .

Elemental analysis of the compound having the formula (105) and having the empirical formula  $C_{22}H_{23}MnN_2O_4$ .

20 1.9 $H_2O$  gives:

Req.%	C 56.4;	H 5.8;	N 6.0;	$H_2O$ 7.3;	Mn 11.7.
Found %	C 56.2;	H 5.8;	N 5.9;	$H_2O$ 7.3;	Mn 11.5.

25

Example 6 (compound 106):

$R_1$  is  $CH_3$ ;  $R_5$  is H; Y is  $-CH_2CH_2-$ ; and A is Cl.

Elemental analysis of the compound having the formula (106) and having the empirical formula  $C_{18}H_{18}ClMnN_2O_4$

30 gives:

Req.%	C 56.2;	H 4.7;	N 7.3;	Mn 17.3.
Found %	C 56.3;	H 4.6;	N 7.1;	Mn 17.1.

35

Example 7 (compound 107):

$R_1$  is  $CH_3$ ;  $R_5$  is  $CH_3$ ; Y is  $-CH_2CH_2-$ ; and A is Cl.

Elemental analysis of the compound having the formula (107) and having the empirical formula  $C_{20}H_{22}ClMnN_2O_4$ .

4.25  $H_2O$ .0.33 NaCl gives:

Req.%	C 49.1;	H 5.8;	N 5.72;	Cl 9.65;	Mn 11.23.
Found %	C 49.1;	H 5.9;	N 5.6;	Cl 9.8;	Mn 10.8.

40

Example 8 (compound 108):

45  $R_1$  is H;  $R_5$  is  $SO_3Na$ ; Y is  $-CH_2CH_2-$ ; and A is Cl.

Elemental analysis of the compound having the formula (108) and having the empirical formula  $C_{16}H_{12}ClMnN_2Na_2O_8S_2 \cdot 3H_2O$ . 1.2NaCl gives:

Req.%	C 28.0;	H 2.6;	N 4.1;	Mn 8.0;	S 9.3.
Found %	C 28.0;	H 2.6;	N 4.1;	Mn 7.8;	S 9.1.

50

Example 9 (compound 109):

55  $R_1$  is H;  $R_5$  is  $SO_3Na$ ; Y is  $-CH_2CH_2-$ ; and A is OH.

Elemental analysis of the compound having the formula (109) and having the empirical formula  $C_{16}H_{13}MnN_2Na_2O_9S_2 \cdot 2H_2O$  gives:

Req.%	C 34.2;	H 3.03;	N 5.0;	Mn 9.8.
Found %	C 34.2;	H 3.3;	N 5.6;	Mn 9.3.

5 Example 10 (compound 110):

R<sub>1</sub> is H; R<sub>5</sub> is SO<sub>3</sub>Na; Y is -CH<sub>2</sub>CH<sub>2</sub>-; and A is OCH<sub>3</sub>.

Elemental analysis of the compound having the formula (110) and having the empirical formula C<sub>17</sub>H<sub>15</sub>MnN<sub>2</sub>Na<sub>2</sub>O<sub>9</sub>S<sub>2</sub> gives:

Req.%	C 34.0;	H 2.7;	N 5.0;	Mn 9.9;	S 11.5.
Found %	C 34.8;	H 3.3;	N 5.0;	Mn 10.1;	S 11.2.

15 Example 11 (compound 111):

R<sub>1</sub> is H; R<sub>5</sub> is SO<sub>3</sub>Na; Y is 1,2-cyclohexylene; and A is CH<sub>3</sub>COO.

Elemental analysis of the compound having the formula (111) and having the empirical formula C<sub>22</sub>H<sub>21</sub>MnN<sub>2</sub>Na<sub>2</sub>O<sub>10</sub>S<sub>2</sub> 1.56H<sub>2</sub>O gives:

Req.%	C 39.6;	H 3.6;	N 4.2;	Mn 8.2;	S 9.6.
Found %	C 39.6;	H 4.2;	N 4.9;	Mn 8.7;	S 9.6.

20 Example 12 (compound 112):

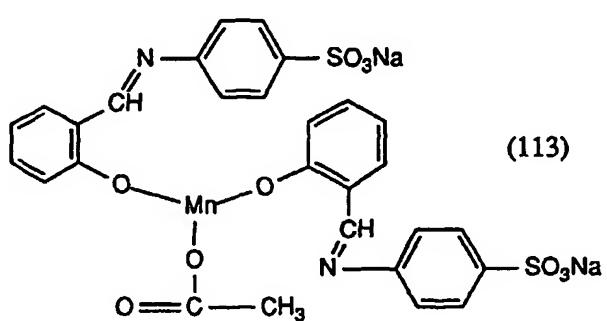
R<sub>1</sub> is H; R<sub>5</sub> is SO<sub>3</sub>Na; Y is 1,2-cyclohexylene; and A is Cl.

Elemental analysis of the compound having the formula (112) and having the empirical formula C<sub>20</sub>H<sub>18</sub>ClMnN<sub>2</sub>Na<sub>2</sub>O<sub>8</sub>S<sub>2</sub> 2.5H<sub>2</sub>O 145NaCl gives:

Req.%	C 32.2;	H 3.1;	N 3.8;	Mn 7.4.
Found %	C 32.2;	H 3.1;	N 3.8;	Mn 7.2.

### Example 13

35 Using the procedure described in Example 1, the following compound of formula (113) is prepared:



50

Elemental analysis of the compound having the formula (113) and having the empirical formula C<sub>28</sub>H<sub>21</sub>MnN<sub>2</sub>Na<sub>2</sub>O<sub>10</sub>S<sub>2</sub> 2.5H<sub>2</sub>O gives:

Req.%	C 44.6;	H 3.4;	N 3.7;	Mn 7.3;	S 8.5.
Found %	C 44.6;	H 4.3;	N 3.8;	Mn 7.9;	S 8.7.

Example 14

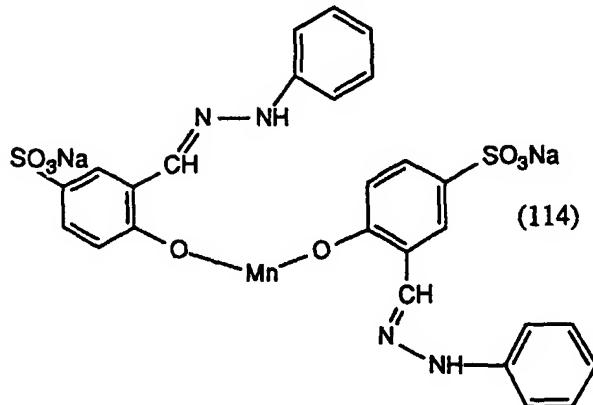
Using the procedure described in Example 1, the following compound of formula (114) is prepared:

5

10

15

20



Elemental analysis of the compound having the formula (114) and having the empirical formula  
25  $C_{26}H_{20}MnN_4Na_2O_8S_2 \cdot 3.45H_2O$  gives:

Req.%	C 42.0;	H 3.65;	N 7.5;	Mn 7.4;	S 8.6.
Found %	C 42.0;	H 4.6;	N 7.4;	Mn 7.4;	S 8.6.

30

Example 15

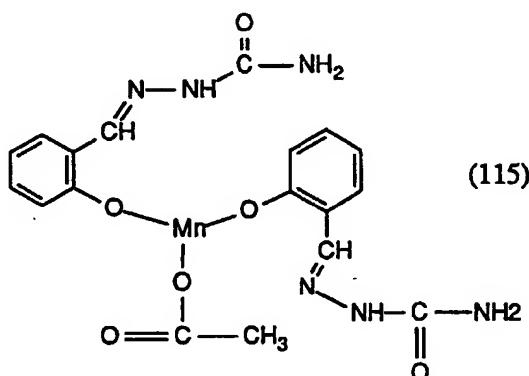
Using the procedure described in Example 1, the following compound of formula (115) is prepared:

35

40

45

50



55

Elemental analysis of the compound having the formula (115) and having the empirical formula  $C_{18}H_{19}MnN_6O_6 \cdot 2.2H_2O$  gives:

Req.%	C 46.7;	H 3.9;	N 20.7;	Mn 13.3.
Found %	C 45.9;	H 4.1;	N 19.5;	Mn 13.3.

### Example 16

Using the procedure described in Example 1, the following compound of formula (116) is prepared:

5



10

Elemental analysis of the compound having the formula (116) and having the empirical formula  $C_7H_5MnNNaO_6S \cdot 2.5H_2O$  gives:

15

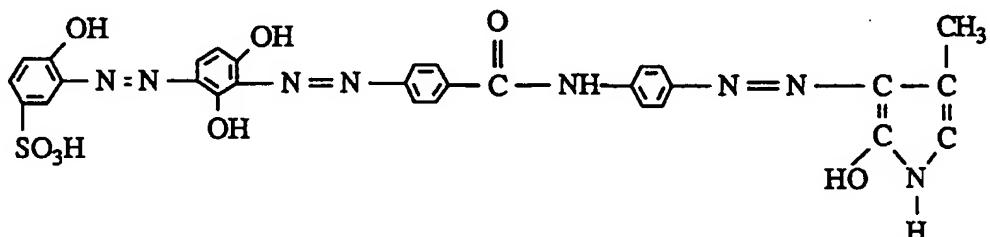
Req.%	C 23.7;	H 2.8;	N 4.0;	Mn 15.7;	S 9.1.
Found %	C 23.7;	H 3.2;	N 3.8;	Mn 14.9.	

### Examples 17 and 18

The re-uptake of dyes, which have become detached from a coloured article during the washing process and re-absorbed on to goods which are also being washed and which are thereby discoloured, is evaluated using a test dye, as follows:

The following commercial brown dyestuff is tested at a concentration of 10 mg per litre of wash liquor:

25



35

There is then added to this wash liquor, with stirring, in a concentration of 7.5 g. per litre of tap water, a detergent having the following composition:

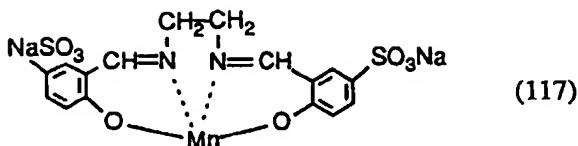
40

6 %	Sodium alkylbenzenesulfonate (®Marlon A375);
5 %	Ethoxylated C <sub>14</sub> -C <sub>15</sub> fatty alcohol (7 moles EO);
3 %	Sodium soap;
30 %	Zeolite A;
7.5 %	Sodium carbonate;
5 %	Sodium metasilicate (5.H <sub>2</sub> O);
43.5 %	Sodium sulphate.

1

The bath is then tested in a "Qlinitest" beaker for 20 minutes at 30°, 40°, 50° or 60°C., respectively. After the addition, with stirring, directly before the treatment, of x% (see Table 1 below) of sodium perborate monohydrate, and/or of y% (see Table 1 below) of the following compound of formula (117), each based on the weight of the above detergent, the appearance of the bath is evaluated visually:

55



10 Table 1

Example	Perborate	Compound (117)	Bath Appearance
	x%	y%	
15	Control	0	dark brown
	Control	2	dark brown
	Control	14	dark brown
	Control	0	dark brown
	Control	0	slight fade
20	17	2	high fade
	18	2	very high fade

25 The ratings are the same after the treatments at each of the four tested temperatures. They show that the combination of perborate and compound (117) causes a significant decomposition of the test dyestuff in the bath. Accordingly, in corresponding washing baths, very little undesired colouration can occur of textiles which are present in the bath, especially with the lower dye bath concentrations used in practice.

26 As is evident from Table 1, this effect cannot be obtained in the absence of compound (117) using concentrations of perborate, e.g., 14% by weight, conventionally used in detergents.

30 Similar results are obtained when the compound of formula (117) is replaced by a compound having one of the formulae (102) to (116).

#### Examples 19 and 20

35 The procedure described in Examples 17 and 18 is repeated except that bleached cotton fabric, in an amount of 50g. per litre of wash bath, is also added.

After the wash treatment, over 20 minutes at 30°C., the fabric pieces are rinsed, dried and quickly ironed and their brightness Y is determined using an ICS SF 500 Spectrophotometer.

40 The difference between the fabric washed without the addition of a dye, and the fabric washed with the addition of the brown dye used in Examples 17 and 18, viz. "ΔY without bleach system" serves as a control rating for the discolouration.

The effectivity of a bleaching system is determined from the equation:

45 Effectivity in % =  $\frac{\Delta Y \text{ without bleach} - \Delta Y \text{ with bleach}}{\Delta Y \text{ without bleach}} \times 100$

The results obtained are set out in Table 2:

50 Table 2

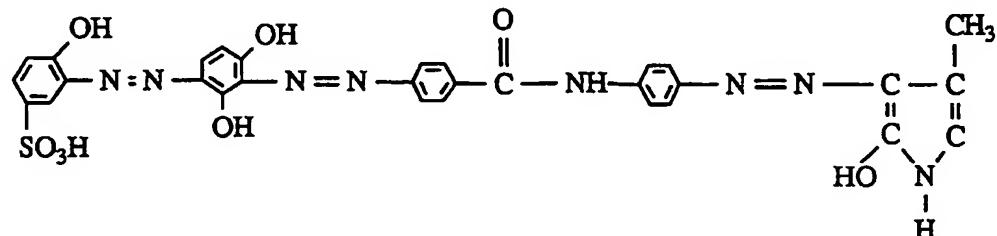
Example	Perborate	Compound (117)	Effectivity
	x%	y%	
Control	0	0	0%
Control	2	0	8%
19	2	0.2	71%
20	2	0.5	76%

Similar results are obtained when the compound of formula (117) is replaced by a compound having one of the formulae (102) to (116).

Likewise, similar results are obtained when Example 19 is repeated except that the brown dyestuff of formula:

5

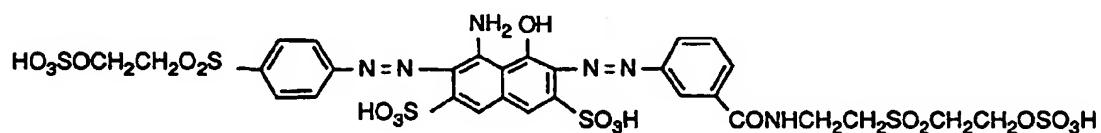
10



15

is replaced by one of the following dyestuffs:

20

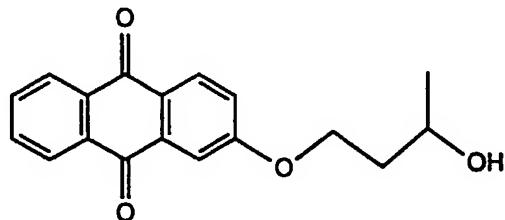


25

or

30

35



40

#### Examples 21 and 22

The procedure described in Examples 19 and 20 is repeated except that percarbonate is used instead of perborate. The results obtained are set out in the following Table 3:

45

50

Table 3

Example	Percarbonate	Compound (117)	Effectivity
	x%	y%	
Control	0	0	0%
Control	2	0	31%
21	2	0.2	61%
22	2	0.5	72%

55

Similar results are obtained when the compound of formula (117) is replaced by a compound having one of the formulae (102) to (116).

Example 23

The procedure described in Examples 19 and 20 is repeated except that there is also added to the bath z% (see Table 4) of polyvinyl pyrrolidone (PVP), as  $\circledast$ Sokalan HP53, having an average molecular weight of about 40,000, based on the weight of the detergent.

5 The results are set out in the following Table 4:

Table 4

10	Example	Perborate	Compound (117)	PVP	Effectivity
		x%	y%	z%	
15	Control	0	0	0	0%
	Control	2	0	0	8%
	23	2	0.2	0.5	78%

Similar results are obtained when the compound of formula (117) is replaced by a compound having one of the formulae (102) to (116).

Example 24

The procedure described in Examples 21 and 22 is repeated except that there is also added to the bath z% (see Table 5) of polyvinyl pyrrolidone (PVP), as  $\circledast$ Sokalan HP53, having an average molecular weight of about 40,000, based on the weight of the detergent.

25 The results are set out in the following Table 5:

Table 5

30	Example	Percarbonate	Compound (117)	PVP	Effectivity
		x%	y%	z%	
	Control	0	0	0	0%
	Control	2	0	0	31%
	24	2	0.2	0.5	74%

35 Similar results are obtained when the compound of formula (117) is replaced by a compound having one of the formulae (102) to (116).

Example 25

40 25g. of bleached cotton fabric are washed for 15 minutes in 200ml. of a bath containing 1.5g. of a detergent having the following composition (ECE standard washing powder):

45	8.0%	Sodium ( $C_{11.5}$ )alkylbenzenesulphonate;
	2.9%	Tallow-alcohol-tetradecane-ethyleneglycoether (14 moles EO);
50	3.5%	Sodium soap;
	43.8%	Sodium triposphosphate;
	7.5%	Sodium silicate;
	1.9%	Magnesium silicate;
	1.2%	Carboxymethylcellulose;
	0.2%	EDTA;
55	21.2%	Sodium sulphate; and
	9.8%	Water.

After rinsing and drying, the fabric is ironed and evaluated spectrophotometrically using an ICS SF 500 Spectrophotometer.

Washing trials at 30°, 60° and 90°C. indicated, in each case, that the resulting spectra are identical in the visible range, viz. between 400 and 700nm, irrespective of whether the trials are conducted with the above detergent tel quel, or with the addition of 0.2% by weight of compound (117).

This confirms the visual findings, i.e. that compound does not exhaust on to, and thus cannot impair the appearance of cotton articles.

The same trials are repeated but using polyamide (Lilion)-tricot or polyester fabric instead of cotton. Again, with these textile types, there is no undesired discolouration of the washed articles by compound (117) itself.

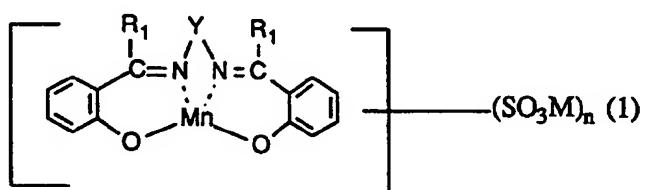
Similar results are obtained when the compound of formula (117) is replaced by a compound having one of the formulae (102) to (116).

10

### Claims

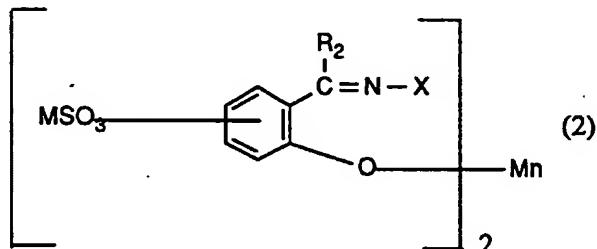
1. A process for inhibiting the re-absorption of migrating dyes in the wash liquor, comprising introducing into a wash liquor containing a peroxide-containing detergent, from 0.5 to 150 mg, per litre of wash liquor, of one or more compounds having the formula (1), (2), (3), (4), (5), (6) or (7):

20



25

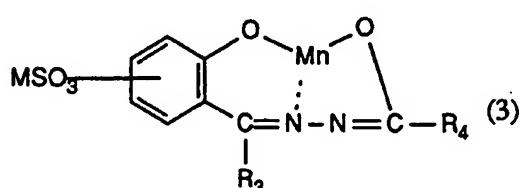
30



35

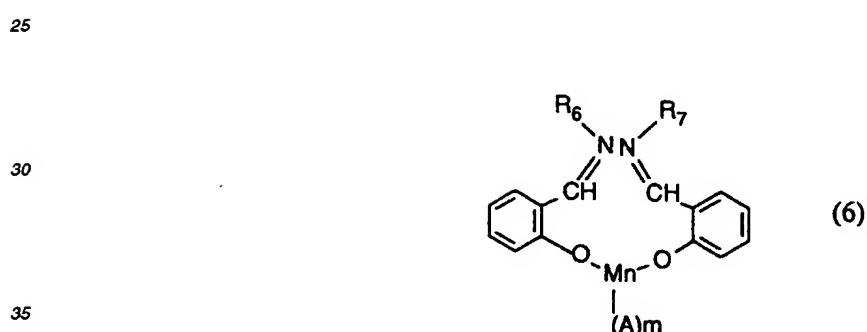
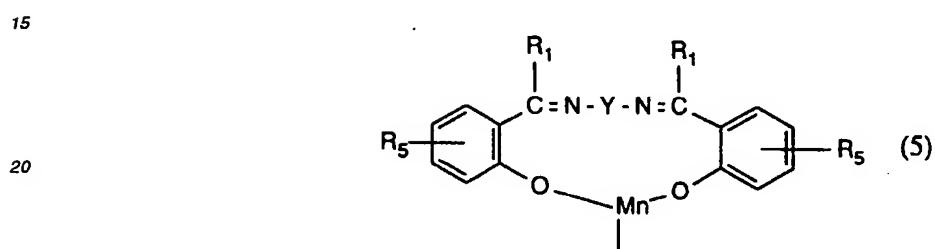
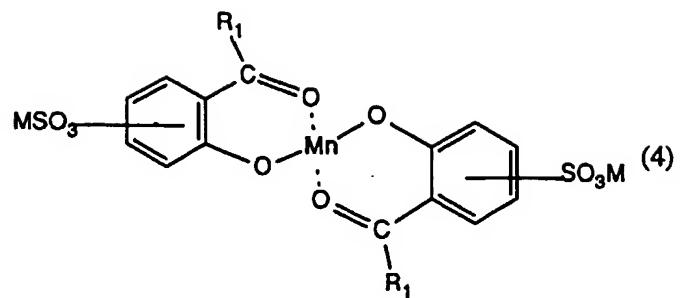
40

45



50

55



or

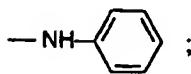


in which R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are the same or different and each is hydrogen or optionally substituted alkyl, cycloalkyl or aryl; R<sub>5</sub> is hydrogen, alkyl or SO<sub>3</sub>M; R<sub>6</sub> and R<sub>7</sub> are the same or different and each is NH-CO-NH<sub>2</sub>, a group of formula

50



or a group of formula



5

Y is optionally substituted alkylene or cyclohexylene; X is OH, NH<sub>2</sub>, optionally substituted aryl or optionally substituted alkyl; n is 0, 1, 2 or 3; M is hydrogen, an alkali metal atom, ammonium or a cation formed from an amine; m is 0 or 1; and A is an anion.

10

2. A process according to claim 1 in which from 1.5 to 75 mg. per litre of wash liquor of one or more compounds having the formula (1), (2), (3), (4), (5), (6) or (7) is introduced into the wash liquor.

15

3. A process according to claim 2 in which from 7.5 to 40 mg. per litre of wash liquor of one or more compounds having the formula (1), (2), (3), (4), (5), (6) or (7) is introduced into the wash liquor.

20

4. A process according to any of claims 1 to 3 in which a compound of formula (1) is used in which R<sub>1</sub> is hydrogen, Y is -CH<sub>2</sub>-CH<sub>2</sub>- , M is sodium and n is 2.

25

5. A process according to any of claims 1 to 3 in which a compound of formula (2) is used in which R<sub>2</sub> is hydrogen and X is OH.

6. A process according to any of claims 1 to 3 in which a compound of formula (3) is used in which R<sub>3</sub> is hydrogen, R<sub>4</sub> is phenyl and the SO<sub>3</sub>M group is in para position with respect to the oxygen atom.

25

7. A process according to any of claims 1 to 3 in which a compound of formula (4) is used in which R<sub>1</sub> is hydrogen and each SO<sub>3</sub>M group is in para position with respect to the oxygen atom.

30

8. A process according to any of claims 1 to 3 in which a compound of formula (5) is used in which R<sub>1</sub> is hydrogen or methyl, R<sub>5</sub> is hydrogen, methyl or SO<sub>3</sub>M, Y is -CH<sub>2</sub>CH<sub>2</sub>- or cyclohexylene and A is a chloride, acetate, hydroxy, methoxy or PF<sub>6</sub> anion.

9. A process according to claim 8 in which R<sub>5</sub> is in para position with respect to the oxygen atom.

35

10. A process according to any of claims 1 to 3 in which a compound of formula (6) is used in which R<sub>6</sub> and R<sub>7</sub> are the same, m is 1 and A is the acetate anion.

11. A detergent composition comprising:

40

- i) 5-90% of A) an anionic surfactant and/or B) a nonionic surfactant;
- ii) 5-70% of C) a builder;
- iii) 0.1-30% of D) a peroxide; and
- iv) 0.005-2% of E) a compound of formula (1), (2), (3), (4), (5), (6) or (7) as defined in claim 1.

45

12. A composition according to claim 11 comprising:

- i) 5-70% of A) an anionic surfactant and/or B) a nonionic surfactant;
- ii) 5-50% of C) a builder;
- iii) 1-12% of D) a peroxide; and
- iv) 0.02-1% of E) a compound of formula (1), (2), (3), (4), (5), (6) or (7) as defined in claim 1.

50

13. A composition according to claim 12 comprising:

- i) 5-70% of A) an anionic surfactant and/or B) a nonionic surfactant;
- ii) 5-40% of C) a builder;
- iii) 1-12% of D) a peroxide; and
- iv) 0.1-0.5% of E) a compound of formula (1), (2), (3), (4), (5), (6) or (7) as defined in claim 1.

14. A composition according to any of claims 11 to 13 comprising a combination of two or more of the compounds of formula (1), (2), (3), (4), (5), (6) or (7) as defined in claim 1.

5 15. A composition according to any of claims 11 to 14 comprising 0.5-5% by weight of a polymer useful in preventing the transfer of labile dyes between fabrics during a washing cycle.

10 16. A composition according to claim 15 comprising 0.2-1.7% of the polymer.

17. A composition according to claim 15 or 16 in which the polymer is a polyvinylpyrrolidone optionally containing an anionic or cationic substituent.

18. A composition according to any of claims 11 to 17 in which the detergent is in powder or granulate form.

19. A composition according to any of claims 11 to 18 in which the detergent is in liquid form and contains 0-5% water.

15 20. A composition according to claim 19 in which the detergent is in liquid form and contains 0-1% water.

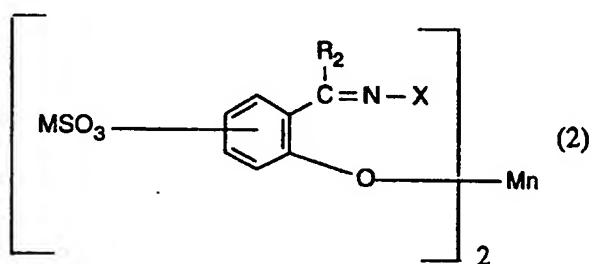
21. A process for the production of a detergent as claimed in claim 18 in which the components of the detergent are mixed in dry form.

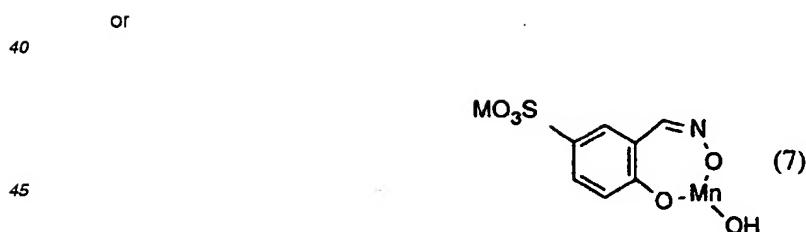
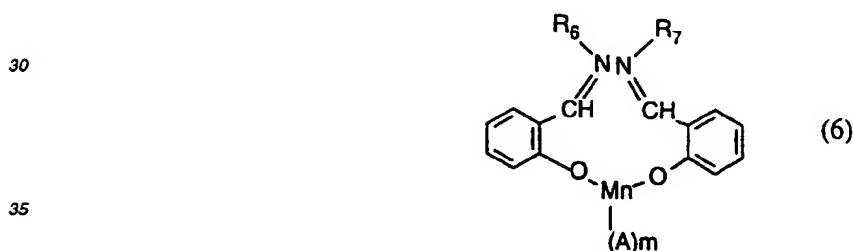
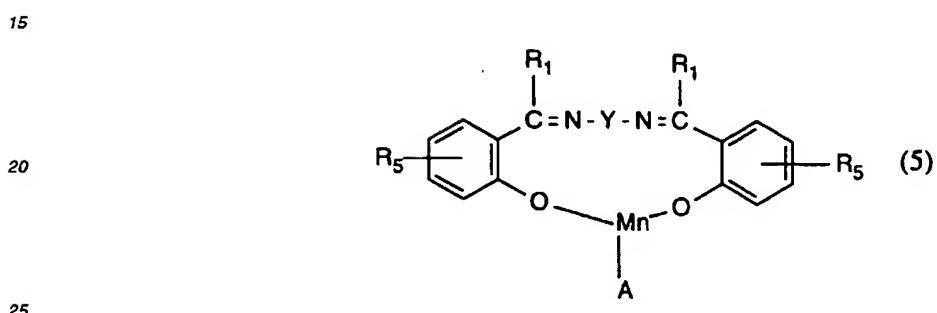
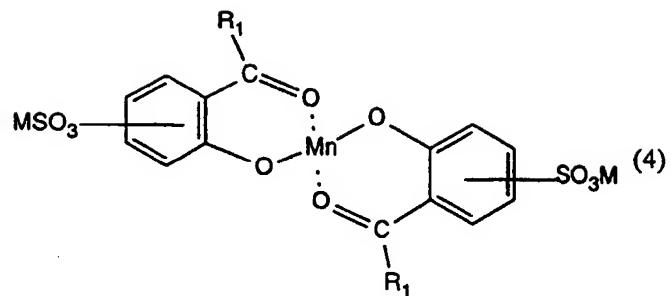
20 22. A process for the production of a detergent as claimed in claim 18 in which a base powder is produced by spray-drying an aqueous slurry which contains all the components defined in claim 11, apart from the components D) and E); and then adding the components D) and E) by dry-blending them into the base powder.

25 23. A process for the production of a detergent as claimed in claim 18 in which the component E) is added to the slurry containing components A), B) and C), which slurry is then spray-dried before component D) is dry-blended into the mixture.

30 24. A process for the production of a detergent as claimed in claim 18 in which component B) is not present, or is only partly present in a slurry containing components A) and C); the component E) is incorporated into component B), which is then added to the spray-dried base powder; and finally component D) is dry-blended into the mixture.

25. A compound having the formula (2), (4), (5), (6) or (7):





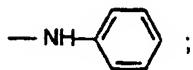
50

in which R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are the same or different and each is hydrogen or optionally substituted alkyl, cycloalkyl or aryl; R<sub>5</sub> is hydrogen, alkyl or SO<sub>3</sub>M; R<sub>6</sub> and R<sub>7</sub> are the same or different and each is NH-CO-NH<sub>2</sub>, a group of formula



or a group of formula

5



10

Y is optionally substituted alkylene or cyclohexylene; X is OH, NH<sub>2</sub>, optionally substituted aryl or optionally substituted alkyl; M is hydrogen, an alkali metal atom, ammonium or a cation formed from an amine; m is 0 or 1; and A is an anion; provided that the following compounds of formula (5) are excluded;

15

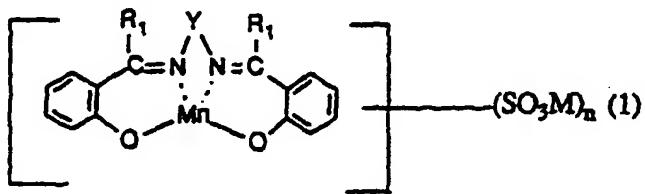
- a) the compounds in which Y is -CH(Ph)-CH(Ph)-, R<sub>1</sub> is H, R<sub>5</sub> is o-t-butyl and A is Cl or PF<sub>6</sub>;
- b) the compounds in which Y is -CH<sub>2</sub>CH<sub>2</sub>-, R<sub>1</sub> is H, R<sub>5</sub> is H and A is Cl or PF<sub>6</sub>; and
- c) the compounds in which Y is cyclohexylene, R<sub>1</sub> is H, R<sub>5</sub> is o-t-butyl and A is an anion.

**Patentansprüche**

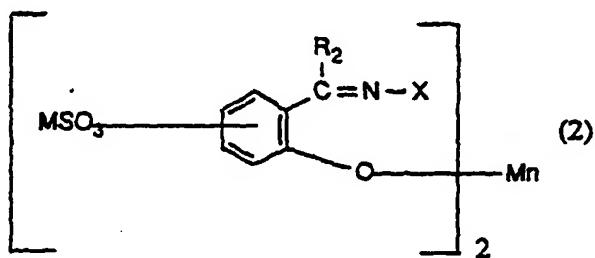
20

1. Verfahren zur Inhibierung der Reabsorption von migrierenden Farbstoffen in der Waschflotte, umfassend das Einbringen in eine ein peroxidhaltiges Waschmittel enthaltende Waschflotte von 0,5 bis 150 mg, pro Liter Waschflotte, einer oder mehrerer Verbindungen der Formel (1), (2), (3), (4), (5), (6) oder (7):

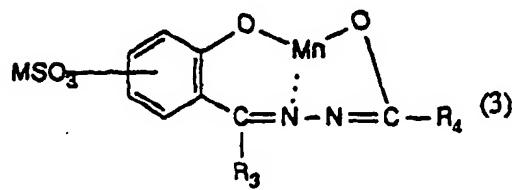
25



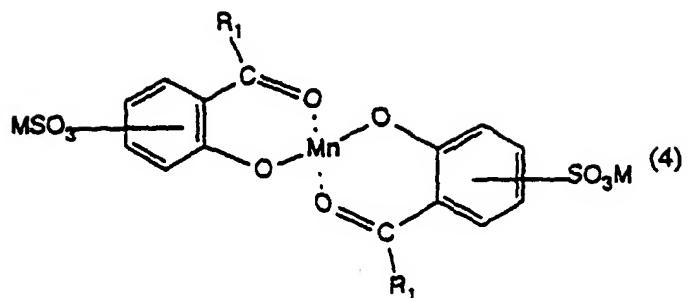
30



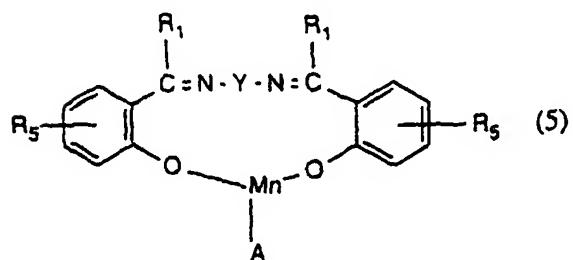
45



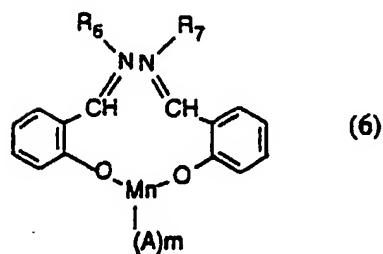
50



15

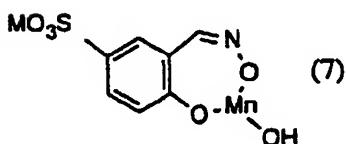


30



oder

40

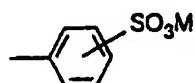


worin

50

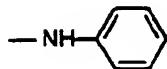
R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> und R<sub>4</sub> gleich oder verschieden sind und jeweils Wasserstoff oder wahlweise substituiertes Alkyl, Cycloalkyl oder Aryl ist; R<sub>5</sub> Wasserstoff, Alkyl oder SO<sub>3</sub>M ist; R<sub>6</sub> und R<sub>7</sub> gleich oder verschieden sind und jeweils NH-CO-NH<sub>2</sub>, eine Gruppe der Formel

55



oder eine Gruppe der Formel

5



ist;

Y wahlweise substituiertes Alkylen oder Cyclohexylen ist; X OH, NH<sub>2</sub>, wahlweise substituiertes Aryl oder wahlweise substituiertes Alkyl ist; n 0, 1, 2 oder 3 ist; M Wasserstoff, ein Alkalimetallatom, Ammonium oder ein von einem Amin gebildetes Kation ist; m 0 oder 1 ist; und A ein Anion ist.

2. Verfahren nach Anspruch 1, wobei 1,5 bis 75 mg, pro Liter Waschflotte, einer oder mehrerer Verbindungen der Formel (1), (2), (3), (4), (5), (6) oder (7) in die Waschflotte eingebracht werden.

15

3. Verfahren nach Anspruch 2, wobei 7,5 bis 40 mg, pro Liter Waschflotte, einer oder mehrerer Verbindungen der Formel (1), (2), (3), (4), (5), (6) oder (7) in die Waschflotte eingebracht werden.

20

4. Verfahren nach mindestens einem der Ansprüche 1 bis 3, wobei eine Verbindung der Formel (1) verwendet wird, worin R<sub>1</sub> Wasserstoff ist, Y -CH<sub>2</sub>-CH<sub>2</sub>- ist, M Natrium ist und n 2 ist.

5. Verfahren nach mindestens einem der Ansprüche 1 bis 3, wobei eine Verbindung der Formel (2) verwendet wird, worin R<sub>2</sub> Wasserstoff ist und X OH ist.

25

6. Verfahren nach mindestens einem der Ansprüche 1 bis 3, wobei eine Verbindung der Formel (3) verwendet wird, worin R<sub>3</sub> Wasserstoff ist, R<sub>4</sub> Phenyl ist und die SO<sub>3</sub>M-Gruppe bezüglich des Sauerstoffatoms in para-Position vorliegt.

30

7. Verfahren nach mindestens einem der Ansprüche 1 bis 3, wobei eine Verbindung der Formel (4) verwendet wird, worin R<sub>1</sub> Wasserstoff ist und jede SO<sub>3</sub>M-Gruppe bezüglich des Sauerstoffatoms in para-Position vorliegt.

8. Verfahren nach mindestens einem der Ansprüche 1 bis 3, wobei eine Verbindung der Formel (5) verwendet wird, worin R<sub>1</sub> Wasserstoff oder Methyl ist, R<sub>5</sub> Wasserstoff, Methyl oder SO<sub>3</sub>M ist, Y-CH<sub>2</sub>CH<sub>2</sub>- oder Cyclohexylen ist und A ein Chlorid- Acetat-, Hydroxy-, Methoxy- oder PF<sub>6</sub>-Anion ist.

35

9. Verfahren nach Anspruch 8, wobei R<sub>5</sub> bezüglich des Sauerstoffatoms in para-Position vorliegt.

10. Verfahren nach mindestens einem der Ansprüche 1 bis 3, wobei eine Verbindung der Formel (6) verwendet wird, worin R<sub>6</sub> und R<sub>7</sub> gleich sind, m 1 ist und A das Acetatanion ist.

40

11. Waschmittelzusammensetzung, umfassend:

- i) 5 - 90 % an A) einem anionischen Tensid und/oder B) einem nichtionischen Tensid;
- ii) 5 - 70 % an C) einem Builder;
- iii) 0,1 - 30 % an D) einem Peroxid; und
- iv) 0,005 - 2 % an E) einer Verbindung der Formel (1), (2), (3), (4), (5), (6) oder (7) wie in Anspruch 1 definiert.

12. Zusammensetzung nach Anspruch 11, umfassend:

- i) 5 - 70 % an A) einem anionischen Tensid und/oder B) einem nichtionischen Tensid;
- ii) 5 - 50 % an C) einem Builder;
- iii) 1 - 12 % an D) einem Peroxid; und
- iv) 0,02 - 1 % an E) einer Verbindung der Formel (1), (2), (3), (4), (5), (6) oder (7) wie in Anspruch 1 definiert.

55

13. Zusammensetzung nach Anspruch 12, umfassend:

- i) 5 - 70 % an A) einem anionischen Tensid und/oder B) einem nichtionischen Tensid;
- ii) 5 - 40 % an C) einem Builder;

iii) 1 - 12 % an D) einem Peroxid; und  
 iv) 0,1 - 0,5 % an E) einer Verbindung der Formel (1), (2), (3), (4), (5), (6) oder (7) wie in Anspruch 1 definiert.

14. Zusammensetzung nach mindestens einem der Ansprüche 11 bis 13, umfassend eine Kombination aus zwei oder mehreren der Verbindungen der Formel (1), (2), (3), (4), (5), (6) oder (7) wie in Anspruch 1 definiert.

15. Zusammensetzung nach mindestens einem der Ansprüche 11 bis 14, umfassend 0,5 - 5 Gew.-% eines Polymeren, das geeignet ist zur Verhinderung der Übertragung labiler Farbstoffe zwischen Textilien während eines Waschzyklus.

16. Zusammensetzung nach Anspruch 15, umfassend 0,2 - 1,7 % des Polymeren.

17. Zusammensetzung nach Anspruch 15 oder 16, wobei das Polymer ein Polyvinylpyrrolidon ist, das wahlweise einen anionischen oder kationischen Substituenten enthält.

18. Zusammensetzung nach mindestens einem der Ansprüche 11 bis 17, wobei das Waschmittel in Pulver- oder Granulatform vorliegt.

19. Zusammensetzung nach mindestens einem der Ansprüche 11 bis 18, wobei das Waschmittel in Flüssigform vorliegt und 0 - 5 % Wasser enthält.

20. Zusammensetzung nach Anspruch 19, wobei das Waschmittel in Flüssigform vorliegt und 0 - 1 % Wasser enthält.

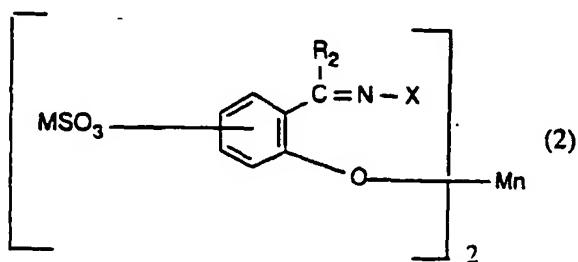
21. Verfahren zur Herstellung eines Waschmittels gemäß Anspruch 18, wobei die Komponenten des Waschmittels in trockener Form vermischt werden.

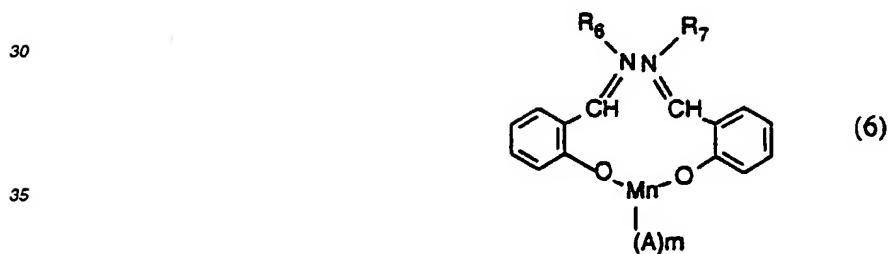
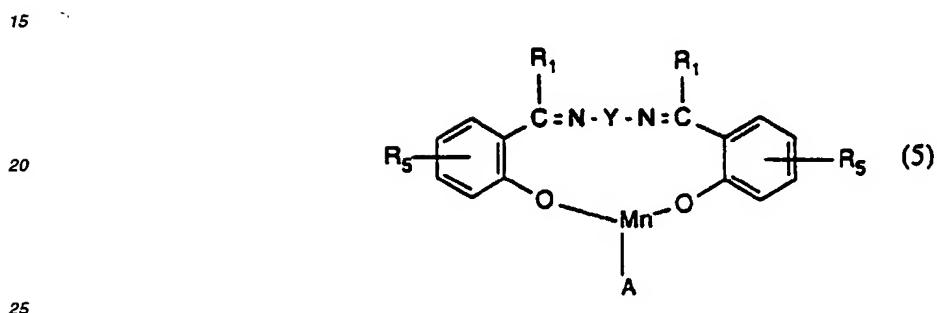
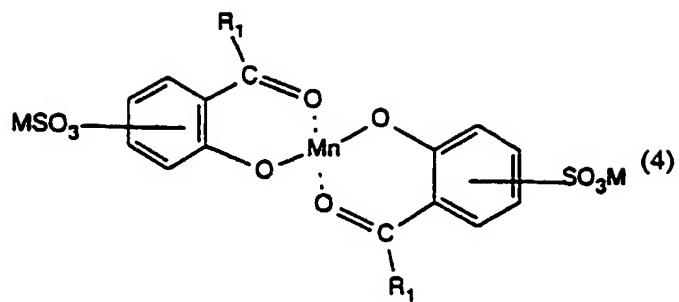
22. Verfahren zur Herstellung eines Waschmittels gemäß Anspruch 18, wobei ein Grundpulver hergestellt wird durch Sprühtrocknen einer wäßrigen Aufschlämmung, welche sämtliche der in Anspruch 11 definierten Komponenten enthält, abgesehen von den Komponenten D) und E); und danach Zugeben der Komponenten D) und E) durch Trockeneinmischen dieser in das Grundpulver.

23. Verfahren zur Herstellung eines Waschmittels gemäß Anspruch 18, wobei die Komponente E) zu der die Komponenten A), B) und C) enthaltenden Aufschlämmung gegeben wird, welche Aufschlämmung dann sprühgetrocknet wird, bevor die Komponente D) in die Mischung trockeneingemischt wird.

24. Verfahren zur Herstellung eines Waschmittels gemäß Anspruch 18, wobei die Komponente B) nicht oder nur teilweise in einer die Komponenten A) und C) enthaltenden Aufschlämmung vorliegt; die Komponente E) in die Komponente B) eingebracht wird, welche dann zu dem sprühgetrockneten Grundpulver gegeben wird; und schließlich die Komponente D) in die Mischung trockeneingemischt wird.

25. Verbindung der Formel (2), (4), (5), (6) oder (7):



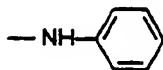


50

worin R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> und R<sub>4</sub> gleich oder verschieden sind und jeweils Wasserstoff oder wahlweise substituiertes Alkyl, Cycloalkyl oder Aryl ist; R<sub>5</sub> Wasserstoff, Alkyl oder SO<sub>3</sub>M ist; R<sub>6</sub> und R<sub>7</sub> gleich oder verschieden sind und jeweils NH-CO-NH<sub>2</sub>, eine Gruppe der Formel



oder eine Gruppe der Formel



5

10

ist; Y wahlweise substituiertes Alkylen oder Cyclohexylen ist; X OH, NH<sub>2</sub>, wahlweise substituiertes Aryl oder wahlweise substituiertes Alkyl ist; M Wasserstoff, ein Alkalimetallatom, Ammonium oder ein von einem Amin gebildetes Kation ist; m 0 oder 1 ist; und A ein Anion ist; mit der Maßgabe, daß die folgenden Verbindungen der Formel (5) ausgenommen sind:

- die Verbindungen, worin Y -CH(Ph)-CH(Ph)- ist, R<sub>1</sub> H ist, R<sub>5</sub> o-t-Butyl ist und A Cl oder PF<sub>6</sub> ist;
- die Verbindungen, worin Y-CH<sub>2</sub>CH<sub>2</sub>- ist, R<sub>1</sub> H ist, R<sub>5</sub> H ist und A Cl oder PF<sub>6</sub> ist; und
- die Verbindungen, worin Y Cyclohexylen ist, R<sub>1</sub> H ist, R<sub>5</sub> o-t-Butyl ist und A ein Anion ist.

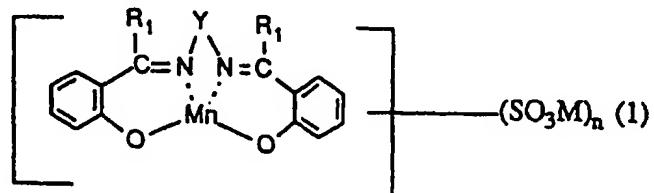
15

#### Revendications

20

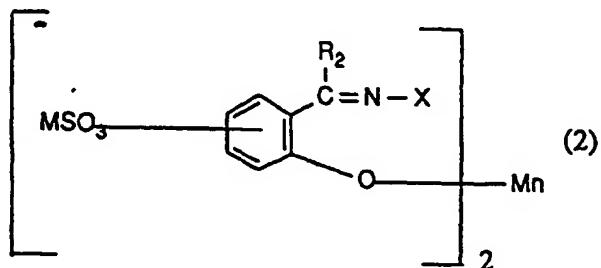
- Procédé d'inhibition de la réabsorption de colorants migrants dans le liquide lessiviel, comprenant l'introduction, dans le liquide lessiviel contenant un détergent renfermant des peroxydes, de 0,5 à 150 mg, par litre de liquide lessiviel, d'un ou de plusieurs composés correspondant aux formules (1), (2), (3), (4), (5), (6) ou (7):

25



30

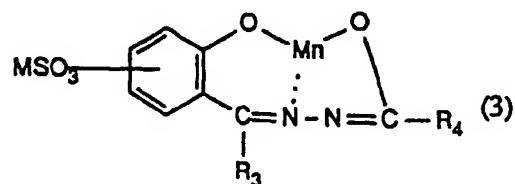
35



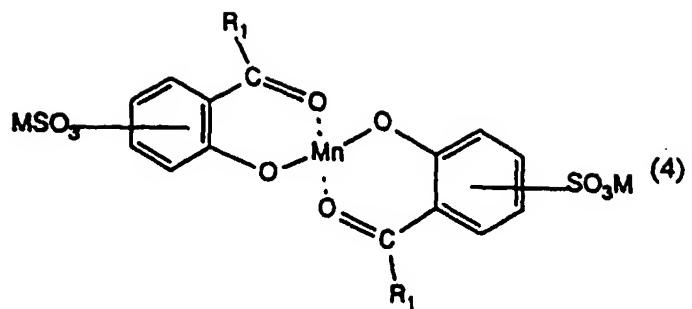
40

45

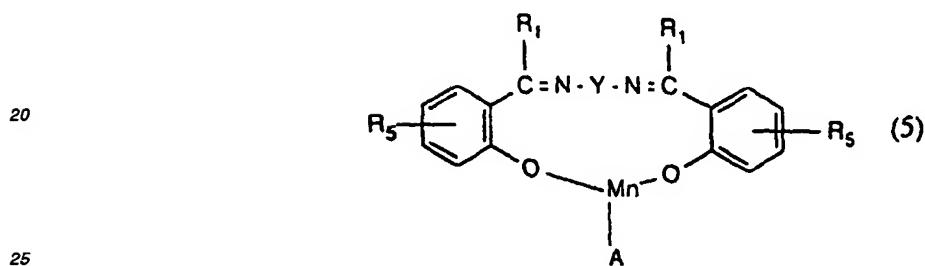
50



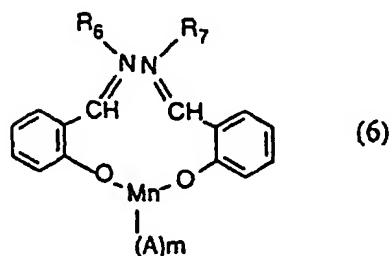
55



15



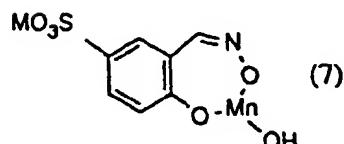
30



35

40

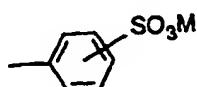
45



dans lesquelles

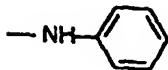
50  $R_1, R_2, R_3$  et  $R_4$ , identiques ou différents, représentent chacun indépendamment, un atome d'hydrogène ou un groupe alkyle, cycloalkyle ou aryle éventuellement substitués,  
 $R_5$  représente un atome d'hydrogène ou un groupe alkyle ou  $SO_3M$ ,  
 $R_6$  et  $R_7$  sont identiques ou différents et chacun représente un groupe  $NH-CO-NH_2$  ou un groupe de formule

55



ou un groupe de formule

5



Y représente un groupe alkylène ou cyclohexylène éventuellement substitué,  
 X est un groupe OH, NH<sub>2</sub>, ou un groupe aryle ou alkyle éventuellement substitués,  
 10 n vaut 0, 1, 2 ou 3,  
 M est un atome d'hydrogène, un ion de métal alcalin, un ion ammonium ou un cation formé par une amine,  
 m vaut 0 ou 1, et  
 A représente un anion.

15 2. Procédé selon la revendication 1, dans lequel on introduit dans le liquide lessiviel de 1,5 à 75 mg par litre de liquide lessiviel, d'un ou de plusieurs composés de formule (1), (2), (3), (4), (5), (6) ou (7).

3. Procédé selon la revendication 2 dans lequel on introduit dans le liquide lessiviel de 7,5 à 40 mg par litre de liquide lessiviel, d'un ou de plusieurs composés de formule (1), (2), (3), (4), (5), (6) ou (7).

20 4. Procédé selon l'une quelconque des revendications 1 à 3 utilisant un composé de formule (1) dans lequel R<sub>1</sub> représente un atome d'hydrogène, Y et un groupe -CH<sub>2</sub>CH<sub>2</sub>-; M est un ion sodium et n vaut 2.

5. Procédé selon l'une quelconque des revendications 1 à 3 utilisant un composé de formule (2) dans lequel R<sub>2</sub> représente un atome d'hydrogène et X un groupe OH.

25 6. Procédé selon l'une quelconque des revendications 1 à 3 utilisant un composé de formule (3) dans lequel R<sub>3</sub> représente un atome d'hydrogène, R<sub>4</sub> un groupe phényle et dans lequel le groupe SO<sub>3</sub>M est en position para par rapport à l'atome d'oxygène.

30 7. Procédé selon l'une quelconque des revendications 1 à 3 utilisant un composé de formule (4) dans lequel R<sub>1</sub> est un atome d'hydrogène et dans lequel chacun des groupes SO<sub>3</sub>M est en position para par rapport à l'atome d'oxygène.

35 8. Procédé selon l'une quelconque des revendications 1 à 3 utilisant un composé de formule (5) dans lequel R<sub>1</sub> représente un atome d'hydrogène ou un groupe méthyle, R<sub>5</sub> représente un atome d'hydrogène ou un groupe méthyle ou SO<sub>3</sub>M, Y est un groupe -CH<sub>2</sub>CH<sub>2</sub>- ou cyclohexylène et A est un ion chlorure, acétate, hydroxy, méthoxy ou PF<sub>6</sub>.

40 9. Procédé selon la revendication 8 dans lequel R<sub>5</sub> est en position para par rapport à l'atome d'oxygène.

10. Procédé selon l'une quelconque des revendications 1 à 3 utilisant un composé de formule (6) dans lequel R<sub>6</sub> et R<sub>7</sub> sont identiques, m vaut 1 et A représente l'ion acétate.

45 11. Composition détergente comprenant

- i) de 5 -90 % d'un agent tensioactif anionique (A) et/ou d'un agent tensioactif non ionique (B);
- ii) de 5 -70 % d'un adjuvant actif ou builder (C);
- iii) de 0,1 à 30 % d'un peroxyde (D), et
- 50 iv) de 0,005 - 2 % d'un composé (E) de formule (1), (2), (3), (4), (5), (6) ou (7) défini dans la revendication 1.

12. Composition selon la revendication 11 comprenant

- i) de 5 -70 % d'un agent tensioactif anionique (A) et/ou d'un agent tensioactif non ionique (B);
- ii) de 5 - 50 % d'un adjuvant actif ou builder (C);
- iii) de 1 à 12 % d'un peroxyde (D), et
- 55 iv) de 0,02 - 1 % d'un composé (E) de formule (1), (2), (3), (4), (5), (6) ou (7) défini dans la revendication 1.

## 13. Composition selon la revendication 12 comprenant

5           i) de 5 -70 % d'un agent tensioactif anionique (A) et/ou d'un agent tensioactif non ionique (B);  
ii) de 5 - 40 % d'un adjuvant actif ou builder (C);  
iii) de 1 à 12 % d'un peroxyde (D), et  
iv) de 0,1 - 0,5 % d'un composé (E) de formule (1), (2), (3), (4), (5), (6) ou (7) défini dans la revendication 1.

## 14. Composition selon l'une quelconque des revendications 11 à 13 comprenant une combinaison de deux ou plusieurs composés de formule (1), (2), (3), (4), (5), (6) ou (7) définis dans la revendication 1.

## 10           15. Composition selon l'une quelconque des revendications 11 à 14 comprenant de 0,5 à 5 % en poids d'un polymère utile dans la prévention du transfert de colorants labiles entre des tissus au cours du lavage.

## 15           16. Composition selon la revendication 15 comprenant de 0,2 à 1,7 % de polymère.

## 17. Composition selon la revendication 15 ou 16 dans laquelle le polymère est une polyvinylpyrrolidone contenant éventuellement un substituant anionique ou cationique.

## 20           18. Composition selon l'une quelconque des revendications 11 à 17 dans laquelle le détergent est sous forme de poudre ou de granulés.

## 25           19. Composition selon l'une quelconque des revendications 11 à 18 dans laquelle le détergent est sous forme liquide et contient de 0 à 5 % d'eau.

## 20           20. Compositon selon la revendication 19 dans laquelle le détergent est sous forme liquide et contient de 0 à 1 % d'eau.

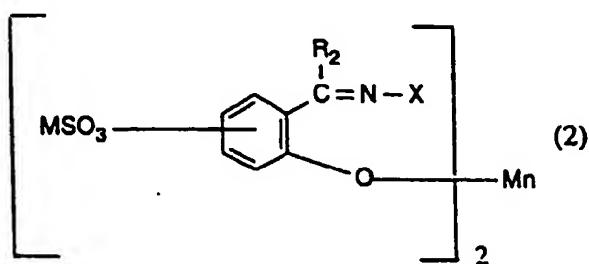
## 25           21. Procédé de préparation d'un détergent conforme à la revendication 18 dans lequel on mélange à sec les composants du détergent.

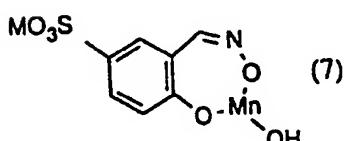
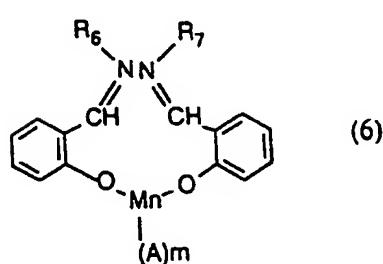
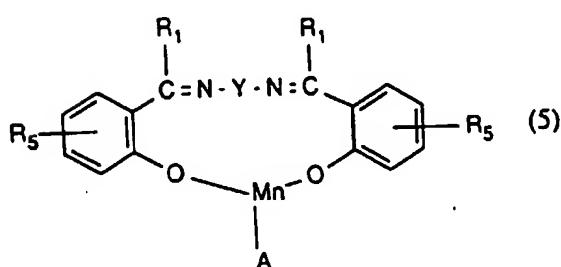
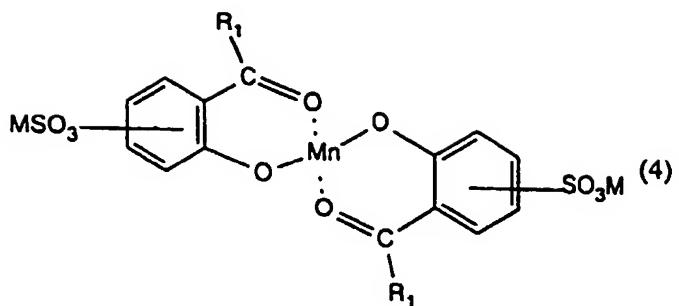
## 30           22. Procédé de préparation d'un détergent selon la revendication 18 dans lequel on prépare une poudre de base par séchage par pulvérisation d'une suspension aqueuse contenant tous les composants définis dans la revendication 11 à l'exception des composants (D) et (E), puis addition des composants (D) et (E) par mélange à sec avec la poudre de base.

## 35           23. Procédé de préparation d'un détergent selon la revendication 18 dans lequel on ajoute le composant (E) à la suspension contenant les composants (A), (B) et (C), laquelle suspension est ensuite séchée par pulvérisation avant qu'on lui incorpore le composant (D) à sec.

## 40           24. Procédé de préparation d'un'détergent selon la revendication 18 dans lequel le composant (B) est absent, ou est présent seulement en partie dans une suspension contenant les composants (A) et (C), le composant (E) est incorporé dans le composant (B) lequel est ensuite ajouté à la poudre de base obtenu par séchage par pulvérisation, puis à la fin le composant (D) est incorporé à sec dans ce mélange.

## 45           25. Composé correspondant à une des formules (2), (4), (5), (6) ou (7) :



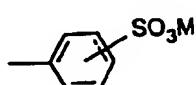


dans lesquelles

R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> et R<sub>4</sub>, identiques ou différents, représentent chacun indépendamment, un atome d'hydrogène ou un groupe alkyle, cycloalkyle ou aryle éventuellement substitués,

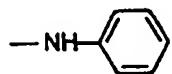
R<sub>5</sub> représente un atome d'hydrogène ou un groupe alkyle ou SO<sub>3</sub>M,

R<sub>6</sub> et R<sub>7</sub> sont identiques ou différents et chacun représente un groupe NH-CO-NH<sub>2</sub> ou un groupe de formule



ou un groupe de formule

5



Y représente un groupe alkylène ou cyclohexylène éventuellement substitué,  
 X est un groupe OH, NH<sub>2</sub>, ou un groupe aryle ou alkyle éventuellement substitués,  
 10 n vaut 0, 1, 2 ou 3,  
 M est un atome d'hydrogène, un ion de métal alcalin, un ion ammonium ou un cation formé par une amine,  
 m vaut 0 ou 1, et  
 A représente un anion,

15 à l'exclusion des composés suivants de formule (5) :

- les composés dans lesquels Y est un groupe -CH(Ph)-CH(Ph)-, R<sub>1</sub> est un atome d'hydrogène, R<sub>5</sub> est un groupe *tert*-butyle en position *ortho* et A est un atome de chlore ou un groupe PF<sub>6</sub>;
- b) les composés dans lesquels Y est un groupe -CH<sub>2</sub>CH<sub>2</sub><sup>-</sup>, R<sub>1</sub> est un atome d'hydrogène, R<sub>5</sub> est un atome d'hydrogène et A est un atome de chlore ou un groupe PF<sub>6</sub>; et
- c) les composés dans lesquels Y est un groupe cyclohexylène, R<sub>1</sub> est un atome d'hydrogène R<sub>5</sub> est un groupe *tert*-butyle en *ortho* et A est un anion.

25

30

35

40

45

50

55